Homework #7, PHY 674, 25 October 1995

Problem X31:

Most elemental (group IV) and compound (III-V and II-VI) semiconductors crystallize in three different crystal structures: In the diamond structure (with point group $O_h = O \times i$), the zincblende structure (with point group T_d), and the Wurtzite structure (with point group C_{6v}). Find how electronic states with angular momentum quantum numbers $l = 0, 1, 2, 3, 4$ split under the crystal field for each of the three crystal structures. (4 points)

Solution:

The characters of the representations belonging to electronic states with angular momentum l have the following form

$$\chi_l^{(+)}(R_\phi) = \frac{\sin\left(l+\frac{1}{2}\right)\phi}{\sin\frac{1}{2}\phi} \times \left|\det(R_\phi)\right| \tag{1}$$

for an even representation belonging to even l and

$$\chi_l^{(-)}(R_\phi) = \frac{\sin\left(l+\frac{1}{2}\right)\phi}{\sin\frac{1}{2}\phi} \times \det(R_\phi) \tag{2}$$

for an odd representation belonging to an odd l.

For the group O_h, we copy the character table from Bouckaert, Smoluchowski, and Wigner (or Joshua, page 83, or Bassani, page 11), and add the characters for the atomic states belonging to angular momentum l according to the formula given above (see Bassani, page 22).

O_h	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3\sigma_h$	$6S_4$	$6\sigma_d$	$8S_6$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	1	-1	-1	1
Γ_{12}	2	2	0	0	-1	2	2	0	0	-1
Γ'_{15}	3	-1	1	-1	0	3	-1	1	-1	0
Γ'_{25}	3	-1	-1	1	0	3	-1	-1	1	0
Γ'_1	1	1	1	1	1	-1	-1	-1	-1	-1
Γ'_2	1	1	-1	-1	1	-1	-1	1	1	-1
Γ'_{12}	2	2	0	0	-1	-2	-2	0	0	1
Γ_{15}	3	-1	1	-1	0	-3	1	-1	1	0
Γ_{25}	3	-1	-1	1	0	-3	1	1	-1	0
l=0, even	1	1	1	1	1	1	1	1	1	1
l=1, odd	3	-1	1	-1	0	-3	1	-1	1	0
l=2, even	5	1	-1	1	-1	5	1	-1	1	-1
l=3, odd	7	-1	-1	-1	1	-7	1	1	1	-1
l=4, even	9	1	1	1	0	9	1	1	1	0

There are a few things worth noting in this table: The primes do NOT distinguish between the even and odd representations. The even representations are Γ_1, Γ_2, Γ_{12}, Γ'_{15}, and Γ'_{25}.

It is not clear which representations carry the prime, but note that the scalar and vector representations Γ_1 and Γ_{15} are unprimed.

We can now break up the angular momentum eigenstates into irreducible representations of the cubic group O_h. The result is (compare Bassani, page 23)

$$(l=0,\text{even}) \quad \to \Gamma_1 \tag{3}$$
$$(l=1,\text{odd}) \quad \to \Gamma_{15} \tag{4}$$
$$(l=2,\text{even}) \quad \to \Gamma_{12} \oplus \Gamma'_{25} \tag{5}$$
$$(l=3,\text{odd}) \quad \to \Gamma'_2 \oplus \Gamma_{15} \oplus \Gamma_{25} \tag{6}$$
$$(l=4,\text{even}) \quad \to \Gamma_1 \oplus \Gamma_{12} \oplus \Gamma'_{15} \oplus \Gamma'_{25} \tag{7}$$

Before we go on to do the same for the zinc blende point group T_d, let us look at the compatibility of representations of O_h and T_d. We proceed by deleting all columns in the character table given above for classes which are not elements of T_d.

O_h, T_d	E	$3C_2$	$8C_3$	$6S_4$	$6\sigma_d$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_{12}	2	2	-1	0	0
Γ'_{15}	3	-1	0	1	-1
Γ'_{25}	3	-1	0	-1	1
Γ'_1	1	1	1	-1	-1
Γ'_2	1	1	1	1	1
Γ'_{12}	2	2	-1	0	0
Γ_{15}	3	-1	0	-1	1
Γ_{25}	3	-1	0	1	-1

We see that the following characters are compatible. (This table is called the compatibility table for O_h and T_d.) For completeness, I also include the extra representations here.

O_h	Γ_1, Γ'_2	Γ'_1, Γ_2	$\Gamma_{12}, \Gamma'_{12}$	$\Gamma'_{15}, \Gamma_{25}$	$\Gamma'_{25}, \Gamma_{15}$	Γ_6^+, Γ_7^-	Γ_7^+, Γ_6^-	Γ_8^+, Γ_8^-
T_d	Γ_1	Γ_2	Γ_{12}	Γ_{25}	Γ_{15}	Γ_6	Γ_7	Γ_8

We now study how states with a given orbital angular momentum l split in a tetrahedral crystal field with point group T_d. The following table lists the irreducible characters for T_d and the characters of the orbital angular momentum eigenstates. (We note that there is also a different notation where the representations Γ_{15} and Γ_{25} are switched. This table follows the convention of semiconductor physics band structure.)

T_d	E	$3C_2$	$8C_3$	$6S_4$	$6\sigma_d$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
$\Gamma_{12} = \Gamma_3$	2	2	-1	0	0
$\Gamma_{15} = \Gamma_4$	3	-1	0	-1	1
$\Gamma_{25} = \Gamma_5$	3	-1	0	1	-1
l=0, even	1	1	1	1	1
l=1, odd	3	-1	0	-1	1
l=2, even	5	1	-1	-1	1
l=3, odd	7	-1	1	1	1
l=4, even	9	1	0	1	1

We can now break up the angular momentum eigenstates into irreducible representations of the cubic group T_d. (Note that we could also get this result from the compatibility tables.) The result is

$$
\begin{aligned}
(l = 0, \text{even}) &\to \Gamma_1 && (8)\\
(l = 1, \text{odd}) &\to \Gamma_{15} && (9)\\
(l = 2, \text{even}) &\to \Gamma_{12} \oplus \Gamma_{15} && (10)\\
(l = 3, \text{odd}) &\to \Gamma_1 \oplus \Gamma_{15} \oplus \Gamma_{25} && (11)\\
(l = 4, \text{even}) &\to \Gamma_1 \oplus \Gamma_{12} \oplus \Gamma_{15} \oplus \Gamma_{25} && (12)
\end{aligned}
$$

Finally, we have to deal with the Wurtzite structure with point group C_{6v}. Here is the character table, including the characters of the orbital angular momentum eigenstates.

C_{6v}	E	C_2	$2C_3$	$2C_6$	$3\sigma_v$	$3\sigma_d$
$\Gamma_1 = A_1$	1	1	1	1	1	1
$\Gamma_2 = A_2$	1	1	1	1	-1	-1
$\Gamma_3 = B_1$	1	-1	1	-1	1	-1
$\Gamma_4 = B_2$	1	-1	1	-1	-1	1
$\Gamma_5 = E_2$	2	2	-1	-1	0	0
$\Gamma_6 = E_1$	2	-2	-1	1	0	0
l=0, even	1	1	1	1	1	1
l=1, odd	3	-1	0	2	1	1
l=2, even	5	1	-1	1	1	1
l=3, odd	7	-1	1	-1	1	1
l=4, even	9	1	0	-2	1	1

We note that it is easy to distinguish between A_1 (even) and A_2 (odd), and also between E_1 and E_2, since they have different signs for the two-fold rotation class (one element) and the six-fold rotation class (2 elements). However, we cannot distinguish between B_1 and B_2, since symmetry cannot tell the difference between the two inequivalent mirror planes parallel to the six-fold axes. (One of these classes contains the corners of the hexagon, the other one contains mirror planes perpendicular to the former.)

The orbital angular momentum eigenstates break up into the following crystal-field terms (see Bethe, 1929, for a similar discussion studying crystal-field splittings with the group D_6):

$$(l = 0, \text{even}) \quad \rightarrow A_1 \tag{13}$$
$$(l = 1, \text{odd}) \quad \rightarrow A_1 \oplus E_1 \tag{14}$$
$$(l = 2, \text{even}) \quad \rightarrow A_1 \oplus E_1 \oplus E_2 \tag{15}$$
$$(l = 3, \text{odd}) \quad \rightarrow A_1 \oplus B_1 \oplus B_2 \oplus E_1 \oplus E_2 \tag{16}$$
$$(l = 4, \text{even}) \quad \rightarrow A_1 \oplus B_1 \oplus B_2 \oplus E_1 \oplus 2E_2 \tag{17}$$

In case you were wondering: Why does A_2 never show up ? Actually, it comes in for l=6. It is usually true that for some large l the representation Γ_l contains the regular representation of the point group (which in turn contains all irreducible representations).

Problem X32:

Determine the crystal field splittings for electrons with angular momentum quantum numbers $l = 0, 1, 2, 3, 4$ in the high-temperature superconductor $YBa_2Cu_3O_7$ with orthorhombic point group $D_{2h} = D_2 \times i$. Do the same for the tetragonal compound $YBa_2Cu_3O_6$ with point group $D_{4h} = D_4 \times i$. (4 points)

Solution:

We have to start with the character table of D_{2h} (from Tinkham). Note that the subscript g stands for *gerade* (which is German for even) and u stands for *ungerade* (which is German for odd). We add the characters for the orbital angular momentum eigenstates and decompose them into irreducible characters.

D_{2h}	E	C_2^z	C_2^y	C_2^x	I	σ_{xy}	σ_{xz}	σ_{yz}
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	1	−1	−1	1	1	−1	−1
B_{2g}	1	−1	1	−1	1	−1	1	−1
B_{3g}	1	−1	−1	1	1	−1	−1	1
A_u	1	1	1	1	−1	−1	−1	−1
B_{1u}	1	1	−1	−1	−1	−1	1	1
B_{2u}	1	−1	1	−1	−1	1	−1	1
B_{3u}	1	−1	−1	1	−1	1	1	−1
l=0, even	1	1	1	1	1	1	1	1
l=1, odd	3	−1	−1	−1	−3	1	1	1
l=2, even	5	1	1	1	5	1	1	1
l=3, odd	7	−1	−1	−1	−7	1	1	1
l=4, even	9	1	1	1	9	1	1	1

Here is the result:

$$(l = 0, \text{even}) \quad \rightarrow A_g \tag{18}$$
$$(l = 1, \text{odd}) \quad \rightarrow B_{1u} \oplus B_{2u} \oplus B_{3u} \tag{19}$$
$$(l = 2, \text{even}) \quad \rightarrow 2A_g \oplus B_{1g} \oplus B_{2g} \oplus B_{3g} \tag{20}$$
$$(l = 3, \text{odd}) \quad \rightarrow A_u \oplus 2B_{1u} \oplus 2B_{2u} \oplus 2B_{3u} \tag{21}$$
$$(l = 4, \text{even}) \quad \rightarrow 3A_g \oplus 2B_{1g} \oplus 2B_{2g} \oplus 2B_{3g} \tag{22}$$

What is the difference between the A and B representations ? Now we see that the A representations is s-like (scalar), whereas the three B representations form a vector (with the basis functions x, y, and z).

Now we do the same for the group D_{4h}:

D_{4h}	E	$2C_4$	C_2^z	$2C_2'$	$2C_2''$	I	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
l=0, even	1	1	1	1	1	1	1	1	1	1
l=1, odd	3	1	-1	-1	-1	-3	-1	1	1	1
l=2, even	5	-1	1	1	1	5	-1	1	1	1
l=3, odd	7	-1	-1	-1	-1	-7	1	1	1	1
l=4, even	9	1	1	1	1	9	1	1	1	1

We find the following crystal-field terms for D_{4h}:

$$(l = 0, \text{even}) \;\rightarrow A_{1g} \tag{23}$$
$$(l = 1, \text{odd}) \;\rightarrow A_{2u} \oplus E_u \tag{24}$$
$$(l = 2, \text{even}) \;\rightarrow A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g \tag{25}$$
$$(l = 3, \text{odd}) \;\rightarrow A_{2u} \oplus B_{1u} \oplus B_{2u} \oplus 2E_u \tag{26}$$
$$(l = 4, \text{even}) \;\rightarrow 2A_{1g} \oplus A_{2g} \oplus B_{1g} \oplus B_{2g} \oplus 2E_g \tag{27}$$

Problem X33:

Find how the $2j+1$-fold degenerate states of an electron with spin quantum number s=1/2 and total angular momentum j=1/2,3/2,5/2,7/2,9/2 split in a cubic field of symmetry O (4 points). Hint: Use the double-group character table in Joshua (p. 76) or Tinkham (p. 77).

Solution:

Let's start with the character table of the group O. The labelling of the representations is a problem, as usual. We deal with this issue by deleting all primed representations of O_h. (This is the same as throwing out the bottom half of the character table of O_h.) This notation follows Bethe (1929). Next we want to find the extra representations of O. We know that there are three new classes $\bar{E}$, $8\bar{C}_3$, and $6\bar{C}_4$, therefore there are three extra representations called Γ_6, Γ_7, and Γ_8. The sum of squares of their dimensions is 24 (number of barred elements), therefore these dimensions are 2, 2, and 4. We take Γ_6 to be the representation with $j=\frac{1}{2}$ and Γ_8 to be the one corresponding to $j=\frac{3}{2}$. (Of course we have to make sure that these representations are indeed irreducible by checking the inner product of the character with itself.) For Γ_7, this leaves two constants to be determined from orthogonality, the value of the characters at C_4 and C_3. The parity of the orbital angular momentum states (with a given l) is obvious, but a total angular momentum j does not define the parity. We have to consider both cases of parity for each j depending on the orbital angular momentum l from which this state is derived. However, since there is no element with negative determinant in this group, the odd and even representations are the same. (We can set up these representations using the table in Joshua on page 77.)

^dO	E	$3C_4^2$ $3\bar{C}_4^2$	$6C_4$	$6C_2$ $6\bar{C}_2$	$8C_3$	$\bar{E}$	$6\bar{C}_4$	$8\bar{C}_3$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	-1	1
Γ_{12}	2	2	0	0	-1	2	0	-1
Γ_{15}	3	-1	1	-1	0	3	-1	0
Γ_{25}	3	-1	-1	1	0	3	0	0
Γ_6	2	0	$\sqrt{2}$	0	1	-2	$-\sqrt{2}$	-1
Γ_7	2	0	$-\sqrt{2}$	0	1	-2	$\sqrt{2}$	-1
Γ_8	4	0	0	0	-1	-4	0	1
l=0	1	1	1	1	1	1	1	1
l=1	3	-1	1	-1	0	3	1	0
l=2	5	1	-1	1	-1	5	-1	-1
l=3	7	-1	-1	-1	1	7	-1	1
l=4	9	1	1	1	0	9	1	0
$j=\frac{1}{2}$	2	0	$\sqrt{2}$	0	1	-2	$-\sqrt{2}$	-1
$j=\frac{3}{2}$	4	0	0	0	-1	-4	0	1
$j=\frac{5}{2}$	6	0	$-\sqrt{2}$	0	0	-6	$\sqrt{2}$	0
$j=\frac{7}{2}$	8	0	0	0	1	-8	0	-1
$j=\frac{9}{2}$	10	0	$\sqrt{2}$	0	-1	-10	$-\sqrt{2}$	1

The orbital angular momentum eigenstates break up as follows in the crystal field with symmetry O. We see that these crystal-field terms are just like in the group O_h (minus the primes), but different from the terms in T_d. We also break up the total angular momentum representations:

$$l=0 \quad \to \Gamma_1 \tag{28}$$
$$l=1 \quad \to \Gamma_{15} \tag{29}$$
$$l=2 \quad \to \Gamma_{12} \oplus \Gamma_{25} \tag{30}$$
$$l=3 \quad \to \Gamma_2 \oplus \Gamma_{15} \oplus \Gamma_{25} \tag{31}$$
$$l=4 \quad \to \Gamma_1 \oplus \Gamma_{12} \oplus \Gamma_{15} \oplus \Gamma_{25} \tag{32}$$
$$j=\tfrac{1}{2} \quad \to \Gamma_6 \tag{33}$$
$$j=\tfrac{3}{2} \quad \to \Gamma_8 \tag{34}$$
$$j=\tfrac{5}{2} \quad \to \Gamma_7 \oplus \Gamma_8 \tag{35}$$
$$j=\tfrac{7}{2} \quad \to \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 \tag{36}$$
$$j=\tfrac{9}{2} \quad \to \Gamma_6 \oplus 2\Gamma_8 \tag{37}$$

Problem X34:

Find the double groups, classes, and "extra" irreducible representations for the point groups O_h and T_d.

Solution:

For O_h, this is similar to the last problem, but now we have to take into account the inversion also. There are even and odd extra representations. Compare this table with Table I in Elliot, Phys. Rev. **96**, 280 (1954).

${}^dO_h$	E	$3C_4^2$ $3\bar{C}_4^2$	$6C_4$	$6C_2$ $6\bar{C}_2$	$8C_3$	I	$3\sigma_h$ $3\bar{\sigma}_h$	$6S_4$	$6\sigma_d$ $6\bar{\sigma}_d$	$8S_6$	$\bar{E}$	$6\bar{C}_4$	$8\bar{C}_3$	$\bar{I}$	$6\bar{S}_4$	$8\bar{S}_6$
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	1	-1	-1	1	1	-1	1	1	-1	1
Γ_{12}	2	2	0	0	-1	2	2	0	0	-1	2	0	-1	2	0	-1
Γ'_{15}	3	-1	1	-1	0	3	-1	1	-1	0	3	1	0	3	1	0
Γ'_{25}	3	-1	-1	1	0	3	-1	-1	1	0	3	-1	0	3	-1	0
Γ'_1	1	1	1	1	1	-1	-1	-1	-1	-1	1	1	1	-1	-1	-1
Γ'_2	1	1	-1	-1	1	-1	-1	1	1	-1	1	-1	1	-1	1	-1
Γ'_{12}	2	2	0	0	-1	-2	-2	0	0	1	2	0	-1	-2	0	1
Γ_{15}	3	-1	1	-1	0	-3	1	-1	1	0	3	1	0	-3	-1	0
Γ_{25}	3	-1	-1	1	0	-3	1	1	-1	0	3	-1	0	-3	1	0
Γ_6^+	2	0	$\sqrt{2}$	0	1	2	0	$\sqrt{2}$	0	1	-2	$-\sqrt{2}$	-1	-2	$-\sqrt{2}$	-1
Γ_7^+	2	0	$-\sqrt{2}$	0	1	2	0	$-\sqrt{2}$	0	1	-2	$\sqrt{2}$	-1	-2	$\sqrt{2}$	-1
Γ_8^+	4	0	0	0	-1	4	0	0	0	-1	-4	0	1	-4	0	1
Γ_6^-	2	0	$\sqrt{2}$	0	1	-2	0	$-\sqrt{2}$	0	-1	-2	$-\sqrt{2}$	-1	2	$\sqrt{2}$	1
Γ_7^-	2	0	$-\sqrt{2}$	0	1	-2	0	$\sqrt{2}$	0	-1	-2	$\sqrt{2}$	-1	2	$-\sqrt{2}$	1
Γ_8^-	4	0	0	0	-1	-4	0	0	0	1	-4	0	1	4	0	-1
$j=\frac{1}{2}$, even	2	0	$\sqrt{2}$	0	1	2	0	$\sqrt{2}$	0	1	-2	$-\sqrt{2}$	-1	-2	$-\sqrt{2}$	-1
$j=\frac{1}{2}$, odd	2	0	$\sqrt{2}$	0	1	-2	0	$-\sqrt{2}$	0	-1	-2	$-\sqrt{2}$	-1	2	$\sqrt{2}$	1
$j=\frac{3}{2}$, even	4	0	0	0	-1	4	0	0	0	1	-4	0	1	-4	0	1
$j=\frac{3}{2}$, odd	4	0	0	0	-1	-4	0	0	0	1	-4	0	1	4	0	-1
$j=\frac{5}{2}$, even	6	0	$-\sqrt{2}$	0	0	6	0	$-\sqrt{2}$	0	0	-6	$\sqrt{2}$	0	-6	$\sqrt{2}$	0
$j=\frac{5}{2}$, odd	6	0	$-\sqrt{2}$	0	0	-6	0	$\sqrt{2}$	0	0	-6	$\sqrt{2}$	0	6	$-\sqrt{2}$	0
$j=\frac{7}{2}$, even	8	0	0	0	1	8	0	0	0	-1	-8	0	-1	-8	0	-1
$j=\frac{7}{2}$, odd	8	0	0	0	1	-8	0	0	0	-1	-8	0	-1	8	0	1
$j=\frac{9}{2}$, even	10	0	$\sqrt{2}$	0	-1	10	0	$\sqrt{2}$	0	1	-10	$-\sqrt{2}$	1	-10	$-\sqrt{2}$	1
$j=\frac{9}{2}$, odd	10	0	$\sqrt{2}$	0	-1	-10	0	$-\sqrt{2}$	0	1	-10	$-\sqrt{2}$	1	10	$\sqrt{2}$	-1

Now we do the same for the group T_d. The extra characters Γ_6, Γ_7, and Γ_8 are constructed from the extra characters of O_h using the compatibility table (see above). The labelling of Γ_6 and Γ_7 is convention. Here is the character table:

T_d	E	$3C_2$ $3\bar{C}_2$	$8C_3$	$6S_4$	$6\sigma_d$ $6\bar{\sigma}_d$	$\bar{E}$	$8\bar{C}_3$	$6\bar{S}_4$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	1	1	-1
$\Gamma_{12} = \Gamma_3$	2	2	-1	0	0	2	-1	0
$\Gamma_{15} = \Gamma_4$	3	-1	0	-1	1	3	0	-1
$\Gamma_{25} = \Gamma_5$	3	-1	0	1	-1	3	0	1
Γ_6	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$
Γ_7	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$
Γ_8	4	0	-1	0	0	-4	1	0
$j = \frac{1}{2}$, even	2	0	1	$\sqrt{2}$	0	-2	-1	$-\sqrt{2}$
$j = \frac{1}{2}$, odd	2	0	1	$-\sqrt{2}$	0	-2	-1	$\sqrt{2}$
$j = \frac{3}{2}$, even	4	0	-1	0	0	-4	1	0
$j = \frac{3}{2}$, odd	4	0	-1	0	0	-4	1	0
$j = \frac{5}{2}$, even	6	0	0	$-\sqrt{2}$	0	-6	0	$\sqrt{2}$
$j = \frac{5}{2}$, odd	6	0	0	$\sqrt{2}$	0	-6	0	$-\sqrt{2}$
$j = \frac{7}{2}$, even	8	0	1	0	0	-8	-1	0
$j = \frac{7}{2}$, odd	8	0	1	0	0	-8	-1	0
$j = \frac{9}{2}$, even	10	0	-1	$\sqrt{2}$	0	-10	1	$-\sqrt{2}$
$j = \frac{9}{2}$, odd	10	0	-1	$-\sqrt{2}$	0	-10	1	$\sqrt{2}$

Problem X35:

Find the double groups, classes, and "extra" irreducible representations for the point groups D_{2h} and D_{4h}.

Solution:

Let us start with D_{2h}. We copy the character table from above. How many new classes are there ? Well, most symmetry elements are mirror reflections or rotations by 180° which do not give us new classes. The only new classes are therefore $\bar{E}$ and $\bar{I}$. Therefore, we have only two extra representations, one even (Γ_5^+) and one odd (Γ_5^-). They are both two-dimensional, since we have eight extra elements. For completeness, let us add the characters of total angular momentum j (even and odd).

${}^dD_{2h}$	E	C_2^z	C_2^y	C_2^x	I	σ_{xy}	σ_{xz}	σ_{yz}		
		$\bar{C}_s^z$	$\bar{C}_s^y$	$\bar{C}_2^x$		$\bar{\sigma}_{xy}$	$\bar{\sigma}_{xz}$	$\bar{\sigma}_{yz}$	$\bar{E}$	$\bar{I}$
A_g	1	1	1	1	1	1	1	1	1	1
B_{1g}	1	1	-1	-1	1	1	-1	-1	1	1
B_{2g}	1	-1	1	-1	1	-1	1	-1	1	1
B_{3g}	1	-1	-1	1	1	-1	-1	1	1	1
A_u	1	1	1	1	-1	-1	-1	-1	1	-1
B_{1u}	1	1	-1	-1	-1	-1	1	1	1	-1
B_{2u}	1	-1	1	-1	-1	1	-1	1	1	-1
B_{3u}	1	-1	-1	1	-1	1	1	-1	1	-1
Γ_5^+	2	0	0	0	2	0	0	0	-2	-2
Γ_5^-	2	0	0	0	-2	0	0	0	-2	2
$j=\frac{1}{2}$, even	2	0	0	0	2	0	0	0	-2	-2
$j=\frac{1}{2}$, odd	2	0	0	0	-2	0	0	0	-2	2
$j=\frac{3}{2}$, even	4	0	0	0	4	0	0	0	-4	-4
$j=\frac{3}{2}$, odd	4	0	0	0	-4	0	0	0	-4	4
$j=\frac{5}{2}$, even	6	0	0	0	6	0	0	0	-6	-6
$j=\frac{5}{2}$, odd	6	0	0	0	-6	0	0	0	-6	6
$j=\frac{7}{2}$, even	8	0	0	0	8	0	0	0	-8	-8
$j=\frac{7}{2}$, odd	8	0	0	0	-8	0	0	0	-8	8
$j=\frac{9}{2}$, even	10	0	0	0	10	0	0	0	-10	-10
$j=\frac{9}{2}$, odd	10	0	0	0	-10	0	0	0	-10	10

Next, we study D_{4h}. There are 16 new elements and 4 new classes. Therefore, we have four extra representations, two even and two odd. All of them are two-dimensional. There is only one constant that we have to find, the value of the Γ_5^+ character at $2C_4$. It will end up in 16 different places in the table (with the different phases). For proper normalization of the Γ_6^+ character, this constant has to be $\sqrt{2}$.

${}^{d}D_{4h}$	E	$2C_4$	C_2^z $\bar{C}_2^z$	$2C_2'$ $\bar{C}_2'$	$2C_2''$ $\bar{C}_2''$	I	$2S_4$	σ_h $\bar{\sigma}_h$	$2\sigma_v$ $\bar{\sigma}_v$	$2\sigma_d$ $\bar{\sigma}_d$	$\bar{E}$	$2\bar{C}_4$	$\bar{I}$	$2\bar{S}_4$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	1	1	1	1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	-1
E_g	2	0	-2	0	0	2	0	-2	0	0	2	0	2	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	1	1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	1	1	-1	-1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	-1	1
E_u	2	0	-2	0	0	-2	0	2	0	0	2	0	-2	0
Γ_6^+	2	$\sqrt{2}$	0	0	0	2	$\sqrt{2}$	0	0	0	-2	$-\sqrt{2}$	-2	$-\sqrt{2}$
Γ_6^-	2	$\sqrt{2}$	0	0	0	-2	$-\sqrt{2}$	0	0	0	-2	$-\sqrt{2}$	2	$\sqrt{2}$
Γ_7^+	2	$-\sqrt{2}$	0	0	0	2	$-\sqrt{2}$	0	0	0	-2	$\sqrt{2}$	-2	$\sqrt{2}$
Γ_7^-	2	$-\sqrt{2}$	0	0	0	-2	$\sqrt{2}$	0	0	0	-2	$\sqrt{2}$	2	$-\sqrt{2}$
$j=\frac{1}{2}$, even	2	$\sqrt{2}$	0	0	0	2	$\sqrt{2}$	0	0	0	-2	$-\sqrt{2}$	-2	$-\sqrt{2}$
$j=\frac{1}{2}$, odd	2	$\sqrt{2}$	0	0	0	-2	$-\sqrt{2}$	0	0	0	-2	$-\sqrt{2}$	2	$\sqrt{2}$
$j=\frac{3}{2}$, even	4	0	0	0	0	4	0	0	0	0	-4	0	-4	0
$j=\frac{3}{2}$, odd	4	0	0	0	0	-4	0	0	0	0	-4	0	4	0
$j=\frac{5}{2}$, even	6	$-\sqrt{2}$	0	0	0	6	$-\sqrt{2}$	0	0	0	-6	$\sqrt{2}$	-6	$\sqrt{2}$
$j=\frac{5}{2}$, odd	6	$-\sqrt{2}$	0	0	0	-6	$\sqrt{2}$	0	0	0	-6	$\sqrt{2}$	6	$-\sqrt{2}$
$j=\frac{7}{2}$, even	8	0	0	0	0	8	0	0	0	0	-8	0	-8	0
$j=\frac{7}{2}$, odd	8	0	0	0	0	-8	0	0	0	0	-8	0	8	0
$j=\frac{9}{2}$, even	10	$\sqrt{2}$	0	0	0	10	$\sqrt{2}$	0	0	0	-10	$-\sqrt{2}$	-10	$-\sqrt{2}$
$j=\frac{9}{2}$, odd	10	$\sqrt{2}$	0	0	0	-10	$-\sqrt{2}$	0	0	0	-10	$-\sqrt{2}$	10	$\sqrt{2}$

Problem X36:

Find how the $2j+1$-fold degenerate states of an electron with spin quantum number s=1/2 and total angular momentum j=1/2,3/2,5/2,7/2,9/2 split in a field of symmetry O_h, T_d, D_{2h}, D_{4h}.

Solution:

The total angular momentum states (with even and odd parity) break up into irreducible representations of O_h as follows. (Actually, we would not even need the character table to do this. We can derive this from the corresponding rules for O by considering parity.)

$$(j=\tfrac{1}{2},\text{even}) \rightarrow \Gamma_6^+ \tag{38}$$
$$(j=\tfrac{1}{2},\text{odd}) \rightarrow \Gamma_6^- \tag{39}$$
$$(j=\tfrac{3}{2},\text{even}) \rightarrow \Gamma_8^+ \tag{40}$$
$$(j=\tfrac{3}{2},\text{odd}) \rightarrow \Gamma_8^- \tag{41}$$
$$(j=\tfrac{5}{2},\text{even}) \rightarrow \Gamma_7^+ \oplus \Gamma_8^+ \tag{42}$$
$$(j=\tfrac{5}{2},\text{odd}) \rightarrow \Gamma_7^- \oplus \Gamma_8^- \tag{43}$$
$$(j=\tfrac{7}{2},\text{even}) \rightarrow \Gamma_6^+ \oplus \Gamma_7^+ \oplus \Gamma_8^+ \tag{44}$$

$$
\begin{aligned}
(j=\tfrac{7}{2},\text{odd}) &\rightarrow \Gamma_6^- \oplus \Gamma_7^- \oplus \Gamma_8^- && (45)\\
(j=\tfrac{9}{2},\text{even}) &\rightarrow \Gamma_6^+ \oplus 2\Gamma_8^+ && (46)\\
(j=\tfrac{9}{2},\text{odd}) &\rightarrow \Gamma_6^- \oplus 2\Gamma_8^- && (47)
\end{aligned}
$$

Finding the crystal-field terms for T_d (with spin-orbit splitting) is trivial. All we need to do is take our knowledge for O_h and use the compatibility table. Just to make sure, compare with the character table given above. We note that the even states for a given j break up just like in the group O, but the odd states may behave differently.

$$
\begin{aligned}
(j=\tfrac{1}{2},\text{even}) &\rightarrow \Gamma_6 && (48)\\
(j=\tfrac{1}{2},\text{odd}) &\rightarrow \Gamma_7 && (49)\\
(j=\tfrac{3}{2},\text{even}) &\rightarrow \Gamma_8 && (50)\\
(j=\tfrac{3}{2},\text{odd}) &\rightarrow \Gamma_8 && (51)\\
(j=\tfrac{5}{2},\text{even}) &\rightarrow \Gamma_7 \oplus \Gamma_8 && (52)\\
(j=\tfrac{5}{2},\text{odd}) &\rightarrow \Gamma_6 \oplus \Gamma_8 && (53)\\
(j=\tfrac{7}{2},\text{even}) &\rightarrow \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 && (54)\\
(j=\tfrac{7}{2},\text{odd}) &\rightarrow \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 && (55)\\
(j=\tfrac{9}{2},\text{even}) &\rightarrow \Gamma_6 \oplus 2\Gamma_8 && (56)\\
(j=\tfrac{9}{2},\text{odd}) &\rightarrow \Gamma_7 \oplus 2\Gamma_8 && (57)
\end{aligned}
$$

For D_{2h}, this is also very simple, since there is only one pair of extra characters (Γ_5^+ even and Γ_5^- odd). We therefore obtain:

$$
\begin{aligned}
(j=\tfrac{2n-1}{2},\text{even}) &\rightarrow n\Gamma_5^+ && (58)\\
(j=\tfrac{2n-1}{2},\text{odd}) &\rightarrow n\Gamma_5^- && (59)
\end{aligned}
$$

For the group D_{4h}, we find the crystal-field terms by decomposing the characters from the character table:

$$
\begin{aligned}
(j=\tfrac{1}{2},\text{even}) &\rightarrow \Gamma_6^+ && (60)\\
(j=\tfrac{1}{2},\text{odd}) &\rightarrow \Gamma_6^- && (61)\\
(j=\tfrac{3}{2},\text{even}) &\rightarrow \Gamma_6^+ \oplus \Gamma_7^+ && (62)\\
(j=\tfrac{3}{2},\text{odd}) &\rightarrow \Gamma_6^- \oplus \Gamma_7^- && (63)\\
(j=\tfrac{5}{2},\text{even}) &\rightarrow \Gamma_6^+ \oplus 2\Gamma_7^+ && (64)\\
(j=\tfrac{5}{2},\text{odd}) &\rightarrow \Gamma_6^- \oplus 2\Gamma_7^- && (65)\\
(j=\tfrac{7}{2},\text{even}) &\rightarrow 2\Gamma_6^+ \oplus 2\Gamma_7^+ && (66)\\
(j=\tfrac{7}{2},\text{odd}) &\rightarrow 2\Gamma_6^- \oplus 2\Gamma_7^- && (67)\\
(j=\tfrac{9}{2},\text{even}) &\rightarrow 3\Gamma_6^+ \oplus 2\Gamma_7^+ && (68)\\
(j=\tfrac{9}{2},\text{odd}) &\rightarrow 3\Gamma_6^- \oplus 2\Gamma_7^- && (69)
\end{aligned}
$$

Stefan Zollner, A205 Physics, 294-7327, November 2, 1995.